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Composition Studies on Tobacco XXXVI

Changes in Smoke Composition and Filtration by Artificial Alteration of Smoke pH: Vapor Phase Constituents*

by L. Lakritz [1], H. D. Bradley [2], J. H. Terrell [2] and R. L. Stedman [1]

Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture, Philadelphia, Pa., USA [1]

and

Houdry Laboratories, Air Products and Chemicals, Inc., Marcus Hook, Pa., USA [2]

The concept that changes in the patterns of selective filtration or removal of certain smoke constituents can be effected by alteration of smoke pH has been discussed recently (6). Essentially, the concept states that, by altering smoke pH, the proportion of a volatile acidic or basic smoke component in the vapor phase can be increased, making more of the component available for filtration. Data to support this concept were obtained in the case of pyridine and nicotine, although it was evident that physicochemical factors other than simple vapor-particulate partitioning were operative.

The present report extends the previous work in examining the effect of altering smoke pH on certain vapor phase constituents of cigarette smoke. A recent study has shown that the addition of a neutral salt, $NaNO_3$, to cigarettes produces some important changes in vapor phase composition of smoke, including increases in acetonitrile, acetaldehyde and acrolein (7). The addition of acidic or alkaline compounds might be expected to alter the phase partitioning and filtration patterns of such constituents as HCN and H_2S.

METHODS

1. *Cigarettes and Smoking Conditions*

Nonfilter and filter cigarettes with or without additives were prepared as previously described (6). Lactic acid (100 mg./cigarette) was employed as the additive instead of formic acid to obtain the acidic smoke. Dipropylamine (100 mg./cigarette) was employed as the additive to obtain the alkaline smoke. Cigarettes were smoked through a Cambridge filter and the gaseous phase of the fifth puff was analyzed directly by gas chromatography or passed through collection traps using the systems described earlier (4). For each determination, 6—12 cigarettes were analyzed and the averages ± 1 standard deviation were calculated and reported.

2. *Analytical Methods*

Hydrogen, oxygen, carbon monoxide and methane were determined by direct gas chromatography of the vapor phase from the fifth puff on Molecular Sieve 13 × (10 ft. · 0.25 in. column) at ambient temperature (25° C) with thermal conductivity detection. Carbon dioxide, ethylene and ethane were determined on *Polypak-2*** (6 ft. · 0.25 in. column) at ambient temperature with thermal conductivity detection. Methanol, acetaldehyde, acrolein, acetone and acetonitrile were separated and quantitatively analyzed on *Polypak-2* (6 ft. · 0.125 in. column) programmed from 50° C to 170° C (3.5° C per minute), using flame ionization detection. Oxides of nitrogen (5), hydrogen sulfide (4) and hydrogen cyanide (4) were determined colorimetrically by described procedures. Formaldehyde was quantitatively estimated by colorimetric measurement of the reaction product of formaldehyde phenylhydrazone and potassium ferricyanide (4) following collection of the vapor phase in aqueous phenylhydrazine hydrochloride.

The method of *Grob* was used to determine the pH of smoke (2).

RESULTS

In the previous and present studies, dipropylamine was employed as a cigarette additive to produce an alkaline smoke. This base yielded pH values of 8.2, 7.9 and 7.9 for nonfiltered, activated carbon-cellulose acetate filtered and cellulose acetate filtered cigarette smoke, respectively (6). Formic acid was used to produce an acidic

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** Mention of a specific commercial product does not constitute endorsement by the Department over similar items not mentioned.

Table 1 Effect of acidic and basic additives on the composition and filtration of vapor phase constituents in commercial cigarette smoke

	Levels*								
	Nonfilter**			CH filter			CA filter		
Component	None	LA	DPA	None	LA	DPA	None	LA	DPA
H_2	1.7 ± 0.4	1.3 ± 0.4	1.3 ± 0.3	1.1 ± 0.4	1.4 ± 0.6	1.4 ± 0.4	1.2 ± 0.5	1.8 ± 0.4	1.7 ± 0.4
O_2	12 ± 1	13 ± 1	13 ± 1	13 ± 1	14 ± 2	13 ± 1	13 ± 2	11 ± 1	11 ± 1
CO	3.3 ± 0.7	2.6 ± 0.7	3.0 ± 0.7	2.1 ± 0.6	2.7 ± 1.0	3.0 ± 0.8	2.4 ± 0.8	3.5 ± 0.7	3.2 ± 0.5
CO_2	7.5 ± 0.7	6.0 ± 0.8	8.3 ± 0.9	6.4 ± 1.7	6.1 ± 0.9	6.2 ± 1.4	7.2 ± 1.2	4.5 ± 1	7.6 ± 1.3
N oxides	24 ± 3	21 ± 6	25 ± 5	28 ± 6	32 ± 9	33 ± 6	29 ± 7	26 ± 7	33 ± 9
Methane	.54 ± .09	.44 ± .14	.43 ± .08	.41 ± .13	.43 ± .14	.42 ± .09	.38 ± .14	.52 ± .08	.51 ± .08
Ethane	99 ± 14	79 ± 22	120 ± 19	79 ± 29	67 ± 10	72 ± 25	86 ± 21	50 ± 15	110 ± 21
Ethylene	50 ± 9	36 ± 10	61 ± 9	40 ± 16	35 ± 8	41 ± 9	48 ± 12	23 ± 7	54 ± 12
H_2S	4.6 ± 1.2	3.6 ± 1.1	0.6 ± 0.1	0.8 ± 0.2	1.7 ± 0.5	0.1 ± .06	3.5 ± 0.7	3.8 ± 1.2	0.6 ± 0.2
HCN	20 ± 2.9	25 ± 2.9	< 0.2	6.0 ± 2.7	9.7 ± 2.5	< 0.2	15 ± 4.5	27 ± 1.7	< 0.2
HCHO	3.0 ± 0.1	1.9 ± 0.6	1.3 ± 0.4	1.4 ± 0.3	1.7 ± 0.5	0.8 ± 0.1	2.6 ± 0.5	2.2 ± 0.6	1.4 ± 0.2
CH_3CHO	83 ± 16	71 ± 13	63 ± 10	44 ± 11	40 ± 19	30 ± 3	88 ± 7	79 ± 12	73 ± 20
Acrolein	8.0 ± 2.4	8.0 ± 1.8	6.3 ± 1.3	3.4 ± 1.5	2.1 ± 1.3	1.4 ± 0.5	10 ± 2	7.9 ± 1.4	6.6 ± 2.2
Acetone	34 ± 6	33 ± 5	38 ± 4	15 ± 4	10 ± 4	11 ± 1	43 ± 5	32 ± 5	42 ± 10
CH_3CN	13 ± 2	12 ± 1	13 ± 1	4.8 ± 1.3	3.1 ± 0.9	4.2 ± 0.8	12 ± 1.4	9.4 ± 1.3	12 ± 1.8
CH_3OH	16 ± 2	15 ± 4	14 ± 2	5.6 ± 1.7	3.6 ± 1.6	4.1 ± 0.6	21 ± 8	13 ± 4	19 ± 6

* H_2, O_2, CO, CO_2 in vol. %. Ethane and ethylene = ppm x 10^{-1}. All others in micrograms. All data based on 5th puff.
** Average ± 1 standard deviation. CH = activated carbon + cellulose acetate filter, CA = cellulose acetate filter, LA = lactic acid added to cigarette, DPA = dipropylamine added to cigarette. None = no additive.

smoke in the previous study; however, in the present work, lactic acid was employed and this additive yielded a pH value of 4.2 for the smoke from all cigarettes.

Values for 16 vapor phase constituents in the smoke from the various cigarettes are shown in Table 1. The indicated values are averages ± 1 standard deviation. Although somewhat high, the variability of the values was sufficient to permit detection of large compositional differences, which was the primary objective of the work.

1. Permanent gases

The levels of methane, ethane, ethylene, hydrogen, oxygen, carbon monoxide, carbon dioxide and oxides of nitrogen in smoke are not influenced greatly by the pH of the smoke and/or by the filter type. A few values significantly smaller than the controls were observed for some constituents; for example, P values of < 0.05 in the "t" test were obtained for carbon dioxide and ethylene in cellulose acetate filtered smoke from cigarettes with lactic acid. In the main, however, the reductions are relatively small. The failure of the two filter types to remove such components selectively is well known (1). Apparently the acidic and basic cigarette additives do not pyrolyze sufficiently to grossly influence the levels of the oxides of carbon and nitrogen. This agrees with the previous postulation that the additives volatilize to a large extent, giving large increases in total particulate matter and alterations in smoke pH (6).

2. Acidic constituents

In nonfilter cigarettes, the smoke pH influences markedly the level of H_2S in the vapor phase; based on the limits of the standard deviations, a reduction of 79–91 % is obtained with alkaline smoke. A similar pattern is obtained with the alkaline smoke in the filter cigarettes. The combination of an alkaline additive and an activated carbon-cellulose acetate filter gives an overall reduction of about 98 % based on the average value for the nonfilter cigarette without additive.

Although the selective removal of H_2S by charcoal is apparent, filtration *per se* is not primarily responsible for the lower values since the percentage reductions are essentially the same regardless of the filter characteristics. The effect is probably a reflection of partitioning of H_2S between vapor and particulate phases of the smoke in a manner analogous to pyridine and nicotine. Using a value of $K_1 = 5.7 \cdot 10^{-8}$ for H_2S, the theoretical ratio of salt to acid in the smoke from nonfilter cigarettes with dipropylamine (pH 8.2) is 9.1 and the ratio in nonfilter cigarettes without additive (pH 5.6) is 0.023. Therefore, the bulk of H_2S in the alkaline smoke would be expected to occur as the hydrosulfide ion in the particulate matter.

A somewhat similar observation is apparent with HCN. The alkaline smoke shows a large reduction in this compound regardless of the filter used. There appears to be some increase in HCN in smoke from cigarettes containing lactic acid and the cellulose acetate and possibly the multiple filter, but the differences may be statistically questionable in the multiple filter. The effectiveness of the multiple filter in reducing HCN is evident in comparing the cigarettes without additives. The extent of the reduction of HCN in alkaline smoke appears to be greater than that of H_2S. This is not explicable simply on the basis of partitioning effects due to pH. The ionization constant of HCN is $7.2 \cdot 10^{-10}$ so that the proportion of salt to acid at pH 8.2

is much less for HCN than for H_2S. Another contributing factor to the marked reduction of HCN may be cyanohydrin formation with the aldehydes in smoke, which would be accelerated at alkaline pH. One report has appeared on the occurrence in collected smoke of acid-stable cyanide complexes which behave similarly to acetaldehyde cyanohydrin (3); these components are believed to be formed after smoke deposition rather than by pyrolytic generation.

3. Other Constituents

Some reduction of formaldehyde is seen in the smoke from nonfilter cigarettes with acidic or basic additive. However, only the alkaline smoke shows a distinct reduction in the case of filter cigarettes. The results with acetaldehyde and acrolein appear to be less conclusive but some slight reductions may exist. Similar results are apparent with acetone, acetonitrile and methanol. However, the known effectiveness of activated carbon in reducing all of these components is evident in all cases (1).

SUMMARY

The pH of smoke from U.S. commercial cigarettes was varied from 4.2 to 8.2 by the use of acidic and basic cigarette additives. Small reductions or insignificant differences were obtained in the levels of hydrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethane, ethylene and oxides of nitrogen in smoke of varying pH. Reductions of 79–91 % of hydrogen sulfide and more than 90 % of hydrogen cyanide in the vapor phase were obtained by changing the pH from 5.6 to 8.2 in nonfilter cigarettes. Using a activated carbon-cellulose acetate filter with the alkaline smoke, further reductions were obtained for these components. Samples of smoke from cigarettes containing alkaline or acidic additive show some slight reduction in formaldehyde, acetaldehyde, acrolein, acetone, acetonitrile and methanol but the reductions for some of these components may be insignificant.

ZUSAMMENFASSUNG

Durch saure und basische Zusätze zum Tabak wurde im Rauch handelsüblicher amerikanischer Cigaretten eine Änderung des pH-Wertes zwischen 4,2 und 8,2 hervorgerufen. Dadurch kam es nur zu einer geringfügigen Verminderung oder zu unbedeutenden Veränderungen der im Rauch nachweisbaren Mengen an Wasserstoff, Sauerstoff, Kohlenmonoxid, Kohlendioxid, Methan, Äthan, Äthylen und an Stickstoffoxiden. Hingegen führte eine Veränderung des pH-Wertes des Rauches von 5,6 auf 8,2 bei Strangcigaretten in der Gasphase des Rauches zu einer Verminderung des Schwefelwasserstoffes um 79–91 % und des Cyanwasserstoffes um mehr als 90 %. Durch einen Kombinationsfilter aus Zelluloseacetat und aktivierter Kohle wurde im alkalischen Rauch eine weitere Verminderung dieser Verbindungen erreicht. In Rauchproben von Cigaretten mit basischen oder sauren Zusätzen zum Tabak fand sich eine geringfügige Verminderung von Formaldehyd, Acetaldehyd, Akrolein, Azeton, Acetonitril und Methanol, bei einigen dieser Verbindungen ist diese Verminderung aber möglicherweise nicht signifikant.

RÉSUMÉ

Au moyen d'additifs acides ou basiques on a fait varier entre 4,2 et 8,2 le pH de la fumée de cigarettes US du commerce. La modification du pH de la fumée n'a provoqué que des variations faibles ou non significatives des teneurs en H_2, O_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, NO et NO_2. L'élévation de 5,6 à 8,2 du pH de la fumée de cigarettes sans filtres a entraîné une réduction de 79–91 % du taux de H_2S et de plus de 90 % de celui du HCN dans la phase vapeur; si en outre, on utilisait un filtre cellulose-charbon activé, les réductions de ces taux étaient encore plus importantes. Des échantillons de fumée de cigarettes contenant des additifs acides ou alcalins avaient des teneurs légèrement diminuées en formaldéhyde, acétaldéhyde, acroléine, acétone, acétonitrile et méthanol, mais les réductions de certains de ces composants peuvent être non significatives.

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Authors' address:

US Department of Agriculture,
Agricultural Research Service,
Eastern Utilization Research and Development Division,
600 East Mermaid Lane,
Philadelphia, Pennsylvania, 19118, USA

Houdry Laboratories, Air Products and Chemicals, Inc., Marcus Hook, Pa., 19061, USA

C. Beckers Buchdruckerei, Uelzen